Configurationally bistable C center in quenched Si:B: Possibility of a boron-vacancy pair

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The C center is an unusual defect found in ultra-fast-quenched (cw laser irradiated) boron-doped silicon. This center introduces two deep donor-hole traps in the band gap, at $E_V+0.50$ eV (H_1) and $E_V+0.36$ eV (H_2), as revealed by deep-level transient spectroscopy (DLTS). We find that each C center may contribute to either of the two hole-emission signals H_1 and H_2 in a DLTS scan, but not both, and that the one it contributes to depends upon its charge state during sample cooling down to low temperatures. We present a simple double-site configuration-coordinate model of the defect that explains these unusual observations. In this model, the C center can exist in either of two configurations in both of its charge states; each configuration is stable in one charge state. No very large lattice relaxation effect is involved. The C center is then tentatively identified as a boron-vacancy pair (B-V), a defect which has eluded DLTS detection so far. We show how this microscopic model is supported by the results of previous defect studies in ultra-fast-quenched and electron-irradiated silicon. The two donor levels H_1 and H_2 are thus tentatively ascribed to next-nearest- and nearest-neighbor B-V pairs, respectively.

I. INTRODUCTION

Point defects in semiconductors are usually observed in one specific configuration, and in one or several charge states. But they may also exist in two or more configurations, in either one or all of their charge states. The alternate, metastable configurations of a defect can be detected experimentally through their distinct magnetic, optical, or electronic properties, provided their relative populations may be made sufficient.

Electron paramagnetic resonance (EPR) first revealed the existence of such configurationally multistable defects. A prototypical example is the vacancy-oxygen pair $(V\text{-O})^-$ in silicon, observed by Watkins in two excited configurations, $(V\text{-O})^{*-}_{100}$ and $(V\text{-O})^{*-}_{111}$, following low-temperature electron irradiation.[1,2] Later, photocapacitance measurements on deep-level defects demonstrated new examples of such "metastable centers." Thus, the so-called photocapacitance quenching effect in GaAs provided evidence for the existence of a metastable configuration, $(EL_2)^{*0}$, of a dominant defect in this material, the EL_2 center.[3,4] More recently, deep-level transient spectroscopy (DLTS) has been extended to study alternate structures of metastable defects through their representative electronic states.[5] An electron-irradiation-damage defect in InP, the M center, was thus found to exhibit reversible transformations between two configurations, each of which being directly observable by DLTS.[5,6]

The complete understanding of such configurational instabilities has suffered so far from the lack of chemical and structural information about the defects. In most instances it has not been possible to go beyond a phenomenological description of the systems with the help of configuration-coordinate (CC) diagrams. Such CC models, based on large lattice relaxations, have been reported for the above-mentioned EL_2 and M centers,[4,6] although for these two defects, tentative microscopic crystallographic descriptions have also been proposed.[4,7]

We have recently discovered a new configurationally bistable center in silicon using DLTS: two different spectra (each with the same two characteristic defect states, but with different relative magnitudes) were observed for this center, depending upon the electronic and thermal history of the system.[8,9] Unlike the above examples, however, this phenomenon was found to involve a well-identified defect complex in silicon, the interstitial iron-substitutional aluminum pair, Fe_iAl_s. This uniquely enabled us to obtain a detailed microscopic understanding of the configurational bistability. The two defect configurations were shown to correspond to Fe_i sitting in the nearest and next-nearest interstitial sites adjacent to Al_s. The reversible transmutation behavior between the two defect energy levels was explained in terms of single jump motion of Fe_i from one site to the other.

The Fe_iAl_s-pair defect in silicon is also unique in as much as its metastable behavior cannot be considered as a large-lattice-relaxation—related phenomenon. Indeed, all experimental data on this center and its configurational bistability could be simply and consistently accounted for on the basis of a purely electrostatic interaction potential between the two defect constituents, Fe_i and Al_s.[8,9] Such centers may be described with the help of double-site CC diagrams, as schematically shown in Fig. 1. The outstanding feature is the existence of two possible structural arrangements of the defect in both of its charge states. The unusual defect behavior merely arises in this case from the low elastic energy barrier separating the two configurations, which renders them both observable experimentally. Because the total-energy difference between the two configurations is not the same for the two charge states, each configuration introduces a specific energy level in the band gap, and the one which is detected at low temperature depends upon the electronic and thermal history of the system. Fe_iAl_s in silicon corresponds to case

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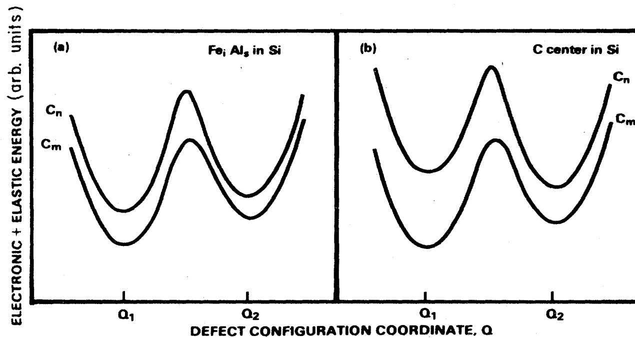

FIG. 1. Double-site CC diagrams for configurationally bistable defects in silicon. The Fe_iAl_s pair (Refs. 8 and 9) belongs to class (a), for which the stable configuration is the same for the two defect charge states, C_m and $C_n(m=n\pm1)$. The C center (this work) corresponds to case (b), where each defect configuration is stable in one charge state.

(a) in Fig. 1, for which the stable configuration is the same for the two defect charge states (nearest-neighbor Fe_i and Al_s).

This paper reports the observation of another configurationally bistable defect in silicon, which can be described by a CC diagram such as (b) in Fig. 1. Here, the stable configuration in one charge state becomes metastable in the other, and vice versa. This implies unique features in the two DLTS spectra characteristic of the center. In the following, this defect will be referred to as the C center. Indeed, to the best of our knowledge, none of the two associated deep levels appears to have been reported so far. The C center was detected following ultra-fast quenching of float-zone-refined boron-doped crystals. Although a definite microscopic identification of the defect is not yet possible on the basis of these sole DLTS data, the properties of the center and the results of previous defect studies in ultra-fast-quenched and electron-irradiated silicon point to the boron-vacancy pair (B-V) as a likely candidate. The two defect configurations are thus tentatively ascribed to the boron atom being a nearest or next-nearest neighbor of the vacancy.

The organization of the paper is as follows. Details on sample preparation and experimental methods are given in Sec. II. The capacitance spectroscopic data on the C center and its configurational bistability are presented in Sec. III. A CC model of the center constructed from these data is then described (Sec. IV). Section V discusses the tentative identification of the C center to the B-V pair, and the paper is summarized in Sec. VI.

II. EXPERIMENTAL DETAILS

The samples used in this study were prepared from boron-doped floating-zone p-type silicon. 10—15-Ω cm, (100)-oriented, wafers obtained from commerical sources, and 5.5-Ω cm, (110)-oriented, slices supplied to us by G. Watkins were used, without difference in the results to be described. No defect levels were found at concentrations higher than $\sim 10^{11}$ cm^{-3} in the samples during preliminary DLTS characterization.

A scanning cw argon-laser irradiation system provided the ultra-fast-quench treatments required to produce the C center. Details on the process and the heat treatments induced in the samples have been given elsewhere.[10,11] Briefly, the laser power is adjusted close to, but below, the level leading to melting (i.e., in the so-called "solid-phase regime"), and the front surface of bare wafers is irradiated by overlapping single-scan laser lines. With the parameters used for this study, the main characteristics of the equivalent furnace anneal treatment are as follows: temperature $\sim$1550 K, duration $\sim$1 msec, and quench rate $\sim 10^6$ K/sec.

The electronic properties of the C center in each configuration, and the configurational transformation kinetics were studied using deep-level transient spectroscopy. All measurements were performed in darkness using the lock-in amplifier technique.[12] The device structures consisted of Schottky-barrier diodes, fabricated at room temperature by evaporation of aluminum through a metal mask.

The procedure used to reveal the configurational instabilities of the M center in InP (Refs. 5—7) and the Fe_iAl_s pair in Si (Refs. 8 and 9) was applied to the study of the C center. The method involves the application or absence of a reverse bias during sample cool down to low temperature (77 K in the present case). This enables to set the defects in the desired charge state in the depletion region of the junction. For a donorlike hole-trapping center as the C center (see Sec. III), cooling the sample with applied reverse bias leaves the defects in the configuration which is stable in the neutral state. Cooling at zero applied bias sets the defects in the stable configuration of the positively charged state. Each configuration may then be analyzed using standard DLTS measurements. The thermally activated configurational transformations can be studied by setting the defects in the desired configuration using the proper cool-down sequence, making this configuration become metastable (by changing the charge state on the defects), and thermally exciting the sample.

III. EXPERIMENTAL RESULTS

A typical DLTS spectrum of the defect states observed following ultra-fast quenching of float-zone (FZ) B-doped silicon is shown in Fig. 2(a). Two major defects labeled H_2 and $H(0.44)$ are detected, with hole-emission activation energies of 0.36 and 0.44 eV, respectively.[13] The shoulder visible on the low-temperature side of $H(0.44)$ reveals the presence of a third weaker signal, which will be denoted as H_1. A strong additional signal, $H(0.10)$, was observed when using large emission-rate windows to record the DLTS spectrum, or scanning the sample temperature from the dopant freeze-out region ($\sim$30 K).

The $H(0.44)$ and $H(0.10)$ levels have been observed previously in Czochralski-grown (CZ) material following similar fast-quench treatment.[14] They were identified as associated with iron impurities, either isolated on interstitial sites (Fe_i), or paired with boron acceptors (Fe_iB_s). Iron is a major contaminant in silicon, and has indeed long been recognized as a dominant thermally induced defect in this material.[15] The H_1 and H_2 levels, in contrast,

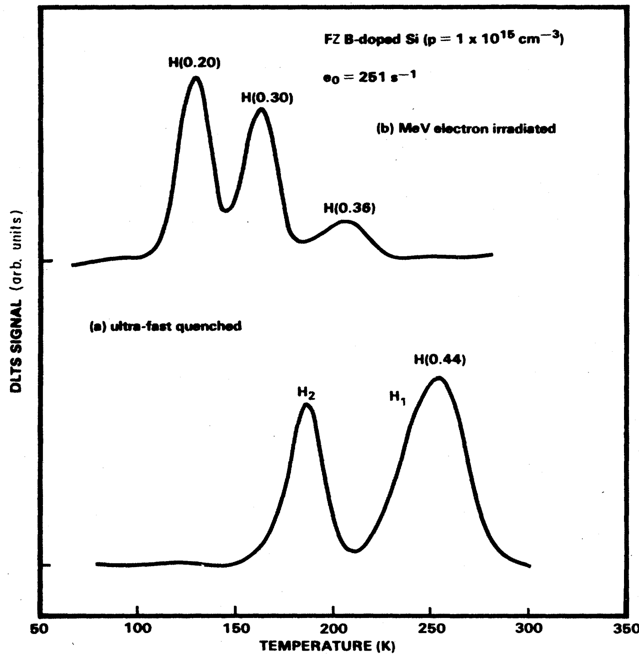

FIG. 2. DLTS spectra for FZ B-doped silicon, following (a) ultra-fast quenching and (b) MeV electron irradiation.

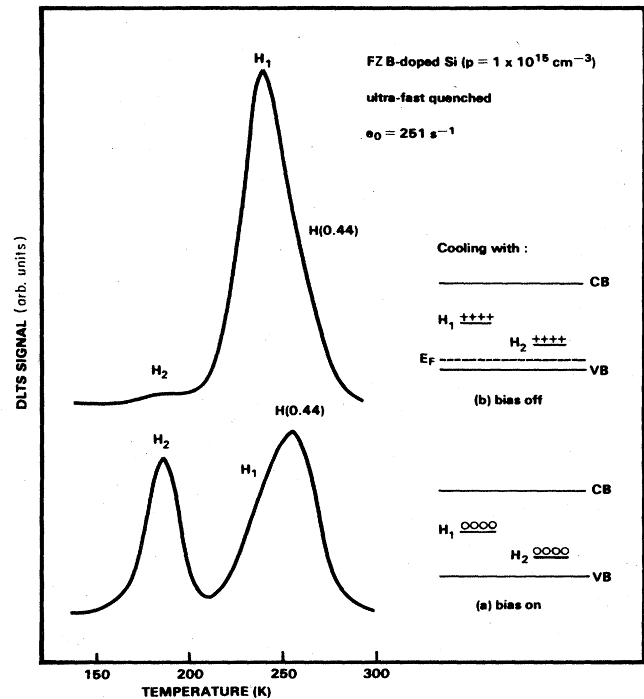

FIG. 3. DLTS spectra for ultra-fast-quenched FZ B-doped silicon, showing the result of cooling with (a) applied reverse bias and (b) zero bias.

were not detected in fast-quenched CZ silicon.[14] In order to test their assignment to well-known radiation-damage defects in silicon, a slice of the same FZ material was irradiated at room temperature with 2-MeV electrons to a fluence of 2×10^{15} electrons cm^{-2}. Figure 2(b) shows the resulting defect-state spectrum, as observed following a 30-min anneal at 50 °C. The spectrum is similar to previously reported ones,[16,17] with three dominant hole traps—$H(0.20)$, $H(0.30)$, and $H(0.36)$—associated with divacancies (VV), carbon interstitials (C_i), and carbon-interstitial—carbon substitutional pairs (C_iC_s), respectively. It turns out that all three levels are distinctly different from the two unidentified quenched-in H_1 and H_2 levels.[18]

The H_1 and H_2 hole traps, which apparently are reported here for the first time, arise from two configurations of a single defect, that we call the C center. This is shown to be true in Fig. 3, which displays the high-energy part ($T>150$ K) of the DLTS spectrum, as recorded following sample cool down under (a) reverse-bias, or (b) zero-bias conditions.[19] The unexpected observation is the dramatic transmutation behavior of the two H_1 and H_2 DLTS peaks: cooling the sample with free holes present causes the extinction of the H_2 signal, and the correlated growth of peak H_1. In contrast, the Fe_i related signal behaves "normally," i.e., is not affected by the type of cool-down sequence used. The $H_1 \leftrightarrow H_2$ transformation was found to be completely reversible: each of the two DLTS spectra characteristic of the C center could be exactly and instantaneously reproduced, provided that the center was cooled from above 300 K in the proper charge state. The transformation could never be driven to completion, however. This is clearly visible on Fig. 3(b), which reveals that about 5% of C centers remain in the configuration (which will be denoted as Q_2) associated with hole emission H_2, following zero-bias sample cool down.

The hole-emission processes from states H_1 and H_2 were studied carefully, after setting the center in the proper configuration. A test for acceptor character was first applied to the two levels by analyzing the effect of increasing junction electric fields on hole-emission rates. None of the two DLTS peaks exhibited the characteristic motion to lower temperatures expected for a Poole-Frenkel effect.[20] We conclude therefore that the two levels are donor levels, with no long-range Coulombic attraction for a hole. The temperature dependence of hole-emission rates was then studied by monitoring the shift in peak positions associated with a change in rate window setting.[12] The results are shown in the Arrhenius plot of Fig. 4. An activation energy of 0.50 eV (respectively, 0.36 eV) is determined for H_1 (respectively, H_2), after correction for the T^2 dependence of the preexponential factor. Finally, the spatial extent of C center production during ultra-fast quenching was explored by measuring the H_2 signal magnitude as a function of the reverse bias or trap-filling pulse voltages supplied to the sample.[12] This measurement was performed following sample cool down under large, applied reverse bias ($V_r=+8$ V), so that all C centers were prepared in configuration Q_2 in the investigated surface region of the material. The C centers were found to be sharply distributed within the first micron: the defect density, which is maximum ~0.5 μm below the surface (concentration $\sim3\times10^{13}$ cm^{-3}), decreases by

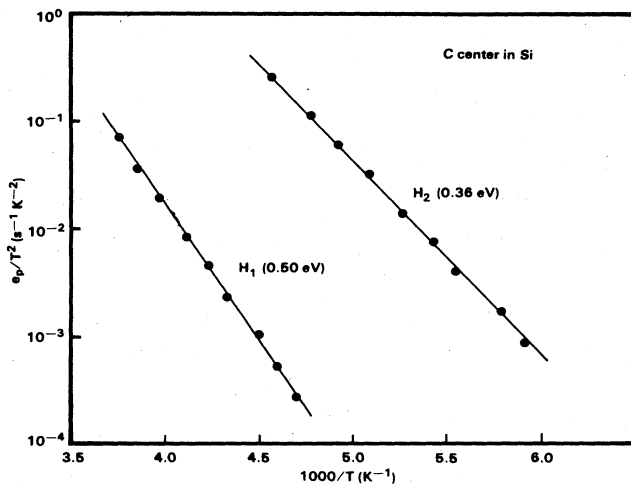

FIG. 4. Thermal emission rate data for the two C-center-associated deep levels in silicon.

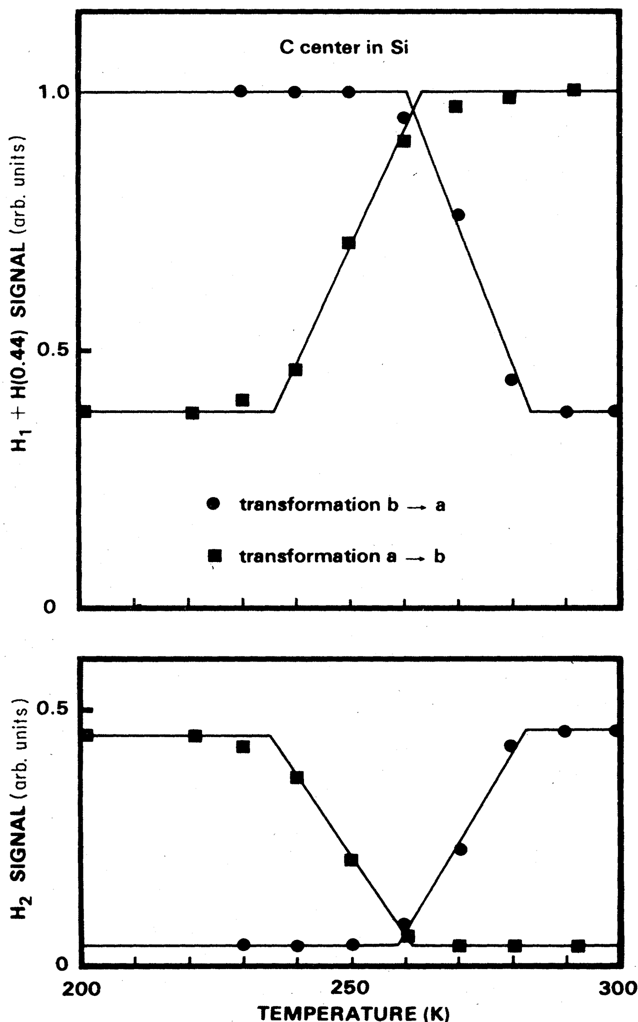

FIG. 5. Isochronal (5 min) annealing data for the transformations $a \rightarrow b$ and $b \rightarrow a$. The DLTS signal at $T=237$ K for $e_0=251$ s^{-1} (see Fig. 3) was used to monitor the changing magnitude of peak H_1 (upper curves). All data points have been normalized to the maximum value of this signal.

an order of magnitude within the next ~ 0.5 μm. It should be pointed out also that a slow decay in H_1 and H_2 signal amplitudes was observed when storing the samples for days at room temperature, indicating that the C center is only marginally stable at 300 K.

The configurational rearrangement of the C center was then investigated quantitatively by studying the thermally activated transformation kinetics between states (a) and (b) of the system, as defined above (see Fig. 3). In order to examine transition $a \rightarrow b$, the sample was first cooled from 300 K to a temperature T under applied reverse bias; then it was annealed for a time t at zero bias, and finally cooled quickly to 77 K. The changing magnitudes of the two emission signals, H_1 and H_2, were used to determine the changing populations of the two defect configurations. A similar procedure was used to examine the reverse transformation, $b \rightarrow a$. State (b) was set at zero bias, and anneals were performed with the bias on.

The anneal temperature T was first varied while keeping time t constant (5 min) to reveal the transformation temperatures. The results of these isochronal anneals are presented in Fig. 5, for both transitions $a \rightarrow b$ and $b \rightarrow a$. The data reveal that both transformations occur in a single stage, but at different temperatures: transition $b \rightarrow a$ takes place at a higher temperature (~ 270 K) than transition $a \rightarrow b$ (~ 245 K). The correlated behavior of the two defect states H_1 and H_2 is confirmed, as is the abovementioned observation that both are never totally destroyed.

The anneal time t was then varied at fixed temperatures T (chosen around the transition temperatures) to explore the configurational transformation rates. The isothermal annealing kinetics were found to be first order. Arrhenius plots for both transitions are shown in Fig. 6. The reaction rates are consistent with the following relations:

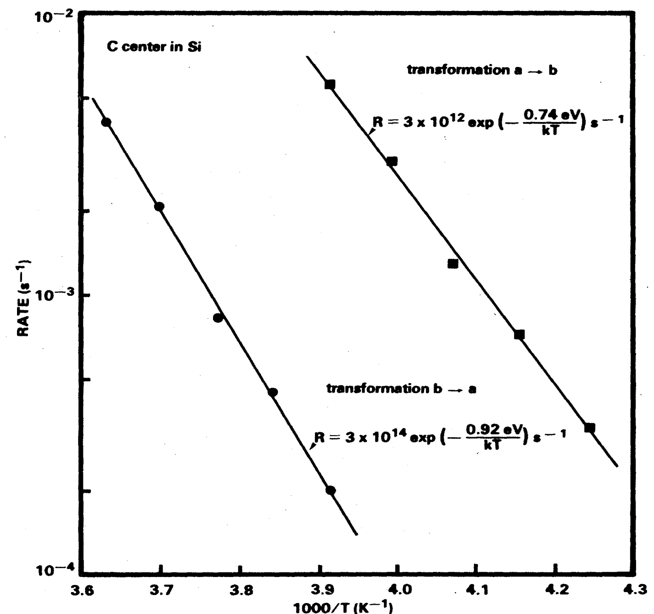

FIG. 6. Arrhenius plots of $a \rightarrow b$ and $b \rightarrow a$ transformation rates.

$$R=(3\times10^{12}\ \mathrm{s}^{-1})\exp\left[-\frac{0.74\ eV}{k_B T}\right]\quad \text{for } a\rightarrow b\ , \quad (1)$$

$$R=(3\times10^{14}\ \mathrm{s}^{-1})\exp\left[-\frac{0.92\ \mathrm{eV}}{k_B T}\right]\quad \text{for } b\rightarrow a\ . \quad (2)$$

IV. CONFIGURATION-COORDINATE MODEL

All the above experimental data relating to the C center and its unusual bistable behavior may be simply explained with the help of a double-site CC diagram such as shown in Fig. 1, i.e., assuming the existence of two possible configurations Q_1 and Q_2 of the center in both of its charge states C^0 and C^+, and an elastic energy barrier separating the two. Then, the two defect emission signals, H_1 and H_2, are simply understood in terms of C^0-C^+ transitions at $Q=Q_1$ and $Q=Q_2$ (we note that this is consistent with the charge-state results presented above), whereas configurational changes $Q_1\leftrightarrow Q_2$ at constant charge on the center account for the observed transmutation behavior, $H_1\leftrightarrow H_2$. The ability to (nearly) completely erase each of the two signals H_1 and H_2 from the DLTS spectrum of the center (Fig. 3) indicates that the stable configuration of the defect is not the same for its two charge states. The CC model which adequately describes the C center is therefore of the type shown as (b) in Fig. 1. Let us remind that for the Fe_iAl_s pair defect in silicon,[8,9] the appropriate CC diagram was of type (a), as revealed by a prominent H_1 emission signal in both DLTS spectra characteristic of the defect (see Fig. 3 in Ref. 9).

The details of the configurational bistability of the C center are best explained using the CC model shown in Fig. 7, constructed from the capacitance spectroscopic data presented in Sec. III. If the diode is cooled to 77 K with reverse bias applied, the two levels of the C center are unoccupied within the extent of the depletion region during the cooling procedure [Fig. 3(a)]. The center is in its neutral-charge state C^0, and the stable configuration Q_2 is populated at low temperature (Fig. 7). As a result, the H_2 donor level associated with this configuration is detected as the dominant DLTS peak [Fig. 3(a)]. But the state of occupancy of the other configuration Q_1 is not zero, because of the low-energy difference between the two configurations;[21] therefore, a small H_1 signal is observed in DLTS [Fig. 3(a)]. If the diode is cooled with the bias off, free holes are captured into the levels, leaving the center in its positive-charge state C^+ [Fig. 3(b)]. The stable configuration of the system is now at $Q=Q_1$, with only a minor fraction of defects occupying the metastable configuration Q_2 at low temperature (Fig. 7); hence the transmutation $H_1\leftrightarrow H_2$ observed during subsequent DLTS characterization of the sample.

The experimentally analyzed $a\rightarrow b$ and $b\rightarrow a$ transformations correspond to the structural rearrangement of the C center towards the steady-state occupancy of the two configurations. Rate $R(a\rightarrow b)$ is controlled by the thermally activated (0.74 eV) configurational change of the positively charged defect (Fig. 7). Similarly, rate $R(b\rightarrow a)$ originates in the energy barrier (0.92 eV) separating Q_1 and Q_2 in the neutral state (Fig. 7). The energy difference between the two barriers explains the difference between the two transformation temperatures noted in the isochronal anneal experiments (Fig. 5). It should be noted also that the preexponential factor in the two transformation rates [Eqs. (1) and (2)] is of the order of a typical lattice vibration frequency (10^{12}—10^{14} s^{-1}). This indicates that the number of defect jumps involved in the structural rearrangement of the center is about unity.

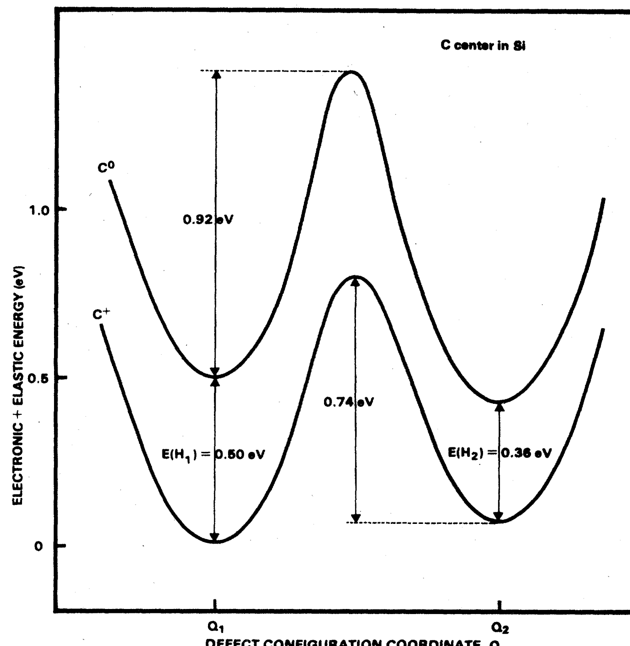

FIG. 7. Configuration coordinate diagram for the C center in silicon. All quoted energies have been determined experimentally. The total-energy difference between the two configurations has been assumed to be the same for C^0 and C^+ (see Ref. 21).

The model just presented for the C center in silicon places it into the more general class of metastable defects in semiconductors, whose unusual properties may be explained using double-site CC diagrams.[9] It is apparent that a complete family of such centers exists in silicon, each with unique features originating in the details of the defect-potential surfaces. Two main classes shown as (a) and (b) in Fig. 1 may be distinguished, with the Fe_iAl_s and C centers as prototypical examples. We have recently shown that the V-O complex in silicon also belongs to this family.[9] Such defects must be considered as "ordinary," from the lattice relaxation point of view.[22] None of the familiar phenomena involving large lattice relaxations, such as large Franck-Condon shifts between thermal and optical ionization energies, would indeed be expected for them.[23] They should therefore be contrasted with previously reported metastable defects in compound semiconductors, which have been described using very large lattice relaxation models.[4,6]

V. MICROSCOPIC MODEL

A more complete description of the C center would require structural information, such as obtained by EPR,

about the two configurations Q_1 and Q_2 observed by DLTS. This is not available at present, so that any microscopic model of the defect, based on the sole DLTS data described in Sec. III, can only be tentative. The arguments supporting the identification of the C center to the B-V pair are presented in the following discussion.

As mentioned previously, the C center has only been observed in ultra-fast-quenched boron-doped FZ silicon. It is neither present in CZ crystals,[14] nor in p-type material (both FZ and CZ) doped with aluminum,[24] following similar heat treatments. This last result strongly suggests the involvement of boron in the defect. To go further, we call upon our knowledge of damage processes in ultra-fast-quenched (cw laser irradiated) silicon. From the results of our extensive studies in this field,[10,11,14,24,25] we expect three kinds of electrically active defects to be produced in FZ B-doped material: (i) transition-metal impurities, either isolated on interstitial sites or paired with boron, (ii) interstitial-related defects, resulting from the interaction of silicon interstitials with impurities at the high laser-induced temperatures, and (iii) vacancy-related defects, arising from vacancy-impurity complexing at high temperature.

Defects belonging to class (i) are indeed detected as the two $H(0.44)$ (Fe_i) and $H(0.10)$ (Fe_iB_s) DLTS signals. We tentatively rule out this first hypothesis for the C center since, to the best of our knowledge, none of two associated levels (H_1 and H_2) identifies any of the deep states reported for well-known transition metals in silicion.[26,27] This is also supported by the sharp distribution of C centers observed below the surface, which contrasts with the smooth profiles previously reported for quenched-in transition metals.[11,24]

We turn to interstitial-related defects, which have eluded DLTS observation so far in fast-quenched material.[14,24,25] These experiments were initially designed to probe silicon interstitial-carbon substitutional complexing at high temperature, through the production of carbon interstitials (C_i) or carbon-interstitial—carbon substitutional pairs (C_iC_s). The results of the complementary electron-irradiation experiments shown in Fig. 2(b) make it clear, however, that the C center does not identify either of these two defects. Boron interstitial (B_i) must be rejected as well, since it is known to anneal out in ~ 30 min at 300 K in p-type material,[28] and to introduce electron traps in the silicon band gap.[29]

The situation regarding vacancy-related defects is very different. We have previously identified phosphorus-vacancy (P-V) and aluminum-vacancy (Al-V) pairs in ultra-fast-quenched P- and Al-doped silicon,[10,24] so that we would expect boron-vacancy pairs to be produced as well in B-doped material. Furthermore, we note that the depth distribution of C centers discussed in Sec. III is very similar to the profiles measured for P-V and Al-V in these previous studies. This would indeed be expected for B-V since, within our proposed model for vacancy-impurity pair production during cw laser irradiation, vacancy in-diffusion from the surface is the limiting process.[10] Finally, within the framework of this model, we estimate the maximum concentration of quenched-in B-V centers to be $\sim 10^{13}$ cm^{-3} in these experiments,[30,31] which compares favorably with the $\sim 3\times 10^{13}$ cm^{-3} measured for the C center (see Sec. III). In view of these circumstantial arguments, the boron-vacancy pair turns out to be the most likely candidate in this tentative microscopic identification of the C center. We now consider whether such identification is consistent with what is known of B-V.

Surprisingly, very limited experimental information on B-V is available in the literature. We are aware of two studied only concerning this defect. Watkins first reported an EPR spectrum, labeled Si-G10, which he tentatively identified as arising from a boron-vacancy pair, the boron atom being in the next-nearest substitutional site from the vacancy.[32] Very recently, an electron-nuclear-double-resonance (ENDOR) study of the Si-G10 spectrum has been performed, providing strong support for Watkins's atomic model.[33] The neutral state of the defect was considered as giving rise to the Si-G10 spectrum, and the requirement of illumination in low-resistivity p-type material to see this resonance as implying a donor state in the gap for B-V, which would be positively charged in low-resistivity material.[32] Our charge-state results on the C center (see Sec. III) are consistent with these predictions.

The one major puzzling result in Watkins's paper is the recovery of the Si-G10 spectrum observed at ~ 260 K, which was ascribed to the annealing of the B-V defect. This point deserves particular attention, since it is in apparent conflict with the observed thermal stability of the C center (days at room temperature). We note, however, that this 260 K annealing temperature coincides with the temperature range where the configurational rearrangement of the C center is observed (see Fig. 5). It is therefore possible to remove this apparent inconsistency in the results by assuming that the recovery of the Si-G10 spectrum is not associated with the annealing of the B-V pair, but with the internal structural rearrangement observed by DLTS. To show the logic of this interpretation, the conditions under which the Si-G10 spectrum was produced must be recalled. The samples studied by Watkins were B-doped ($p \sim 10^{16}$ cm^{-3}) FZ silicon, irradiated with 1.5-MeV electrons at 20.4 K. Upon annealing at ~ 180 K, the vacancy spectrum (Si-G1) was found to disappear and the Si-G10 spectrum to emerge. Upon subsequent anneal, the Si-G10 spectrum disappeared at ~ 260 K. All these observations, coupled to our own data on the C center, may be understood as monitoring the progress of the silicon vacancy towards a substitutional boron atom. At 180 K, the vacancy becomes mobile[34] and diffuses through the lattice, until it comes in second-nearest-neighbor position to a boron atom. It remains trapped there, giving rise to the Si-G10 spectrum: the last diffusion jump towards boron is indeed impeded at this low temperature by the high-energy barrier separating the two sites (see Fig. 7). This final step will await until annealing to ~ 260 K, causing the extinction of the Si-G10 spectrum.

Thus, it appears that the proposed identification of the C center to the B-V pair may be made consistent with Watkins's EPR data on this defect. This in turn strongly suggests that the two configurations observed by DLTS (Q_1 and Q_2 in Fig. 7) correspond to nearest- and next-

nearest neighbor V and B_s. Which configuration is what remains to be determined. Unfortunately, the Fermi-level position and resulting B-V charge state in Watkins's annealing studies are not known. It seems reasonable, however, to assume that these experiments have been conducted in heavily irradiated—hence compensated—material, i.e., with neutral B-V pairs. This would imply that the Si-G10 spectrum arises from configuration Q_1, i.e., that the H_1 and H_2 deep levels are, respectively, associated with second- and first-nearest-neighbor constituents. Our isochronal anneal data for the $b \rightarrow a$ transformation (270 K, 5 min) would then fairly match Watkins's data for the disappearance of the Si-G10 spectrum (260 K, 15 min).

Several experiments should be performed in the future to confirm this identification. The recovery kinetics of the Si-G10 spectrum (under Watkins's experimental conditions) should be studied. If this recovery results from a single-jump vacancy motion as we suggest, the preexponential factor would be expected to be $\sim 10^{13}$ s^{-1}, that of a characteristic vibrational frequency. The thermal stability of the Si-G10 spectrum should also be investigated in lightly irradiated material, i.e., with positively charged B-V pairs. According to the CC model shown in Fig. 7, one would indeed expect the spectrum to be stable at room temperature in this case. DLTS studies should be carried out following similar low-temperature electron irradiations. Search for the C center (as characterized in the present work) in these samples should reveal a critical test for the proposed identification.

Two of our experimental observations remain to be clarified. The first is the nondetection of C centers in room-temperature electron-irradiated material [Fig. 2(b)]. If the proposed microscopic model is correct, one must conclude that boron-vacancy pairing is not significant under such experimental conditions. This could be due to the low boron content ($\sim 10^{15}$ cm^{-3}) of the investigated samples. Alternatively, the B-V pair may be unstable at room temperature in the presence of the high density of electrons and holes generated by irradiation. The second puzzling observation is the nondetection of C centers in ultra-fast-quenched CZ material.[14] This result is indeed unexpected since we know from our previous work[10,24] that in such fast-quench treatments, oxygen (and carbon) impurities do not play a major role as in damage production during electron irradiation. Confirmatory experiments should be carried out on this point, since no simple explanation is available at present.

VI. CONCLUSION

We have reported the discovery of a new configurationally bistable defect in silicon. The C center, as we call it, is observed in float-zone boron-doped material following ultra-fast-quench treatments, such as produced by scanning cw laser irradiation. We have shown that this center can exist in either of two configurations in both of its charge states, and, a unique feature, that each configuration is stable in one of the two charge states. The electronic properties of the two configurations and the kinetics of the reversible configurational transformations have been determined. All data have been organized in a conceptually simple, double-site, CC diagram that explains the unusual properties of the C center.

The C center has been tentatively identified to the boron-vacancy pair. The involvement of boron is suggested by the nondetection of the center in similarly treated aluminum-doped material. The presence of a silicon vacancy is inferred from the apparent vacancy—in-diffusion-limited production of C centers during cw laser irradiation. We have shown that this identification may be made consistent with Watkins's EPR data on B-V, provided that the recovery of the Si-G10 spectrum at ~ 260 K is no longer ascribed to the annealing, but to the configurational rearrangement, of the pair. Within this microscopic model of the C center, the two defect configurations have been tentatively ascribed to the vacancy being a first- or second-nearest neighbor of boron. Experiments have been described, that could help confirm the proposed model. Indeed, an important consequence of this identification would be that the boron-vacancy center is stable at room temperature, contrary to the present belief.

The C center reported in this work adds to the growing list of semiconductor point defects exhibiting configurational bistability. Many examples of such defects, each with distinct unusual properties, have been discovered in the last several years: $EL2$ center in GaAs,[3,4] M center in InP,[5–7] M Fe center in InP,[35] V-O center in Si,[5,9,36] and Fe_iAl_s center in Si.[8,9] These centers may be classified into two main groups, according to whether or not large lattice relaxation effects are needed to understand their properties. It is surprising to note that, to date, the first group corresponds to III-V compounds examples, the second one to silicon examples. A generalized use of the kind of DLTS measurements performed in this study should help discover new configurationally bistable defects. It is an interesting question as to whether the above-mentioned tendency will be confirmed, or if any counterexamples will be found.

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